John von Neumann Institute for Computing


# DFT-MRCI Hybrid Theory

R. Strange, P.J. Knowles

published in

*Modern Methods and Algorithms of Quantum Chemistry*,
J. Grotendorst (Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. **2**, ISBN 3-00-005746-3, p. 40, 2000.



http://www.fz-juelich.de/nic-series/

# DFT-MRCI Hybrid Theory

R. Strange and P. J. Knowles

School of Chemistry, University of Birmingham, Birmingham, B15 2TT. United Kingdom.

Many electronic structure problems are localised in the sense that the important electronic effects that influence a prediction can be viewed as occuring in a small region of space, or a subset of molecular orbitals. We split the overall orbital space of a system into two partitions, $A$ and $B$, where $A$ contains the chemically active orbitals. The spectator partition, $B$, is represented using an inexpensive low-level theory (eg. density functional theory (DFT)). At a cost comparable to that of using a high-level ab initio method, eg. multireference configuration interaction (MRCI), on $A$ alone, we minimise an energy expression for the total system of the form,

$$E_{A\oplus B} = E^{DFT}_{A\oplus B} - E^{DFT}_{A} + E^{MRCI}_{A}.$$

The coupling between $A$ and $B$ arises properly through the variational minimization of the overall energy functional.